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WITNESS my hand this Twenty-ninth day of March 2000

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Radiation Curable Composition.

The invention relates to the formation of water-soluble resin system which will polymerise by UV radiation to produce non-air inhibited films. They consist essentially of cationic salt formed between an amide containing oligomer and an organic acid. The oligomer may include a vinyl or ethylenically unsaturated groups as well as an amide, and this amide is best derived from a secondary amine reacted into the oligomer through a terminal carboxylic acid, an isocyanate or a glycidyl group. The so formed cationic salt, strongly binds the acid radical to this tertiary N of the amide oligomer, rendering it non-volatile and thereby odour free and innocuous, and hence safe to handle.

Background.

Radiation curable inks and coatings have been widely adopted in the field of graphic arts for several decades and are increasingly being applied into other coating applications. The most predominant type of resin systems used, are low volatility acrylic ester or vinyl monomers blended with multifunctional oligomers, for example, epoxy acrylates or urethane acrylates, unsaturated polyester and incorporating a photoinitiator to propagate the anionic polymerisation process once exposed to appropriate UV or EB radiation source. These systems generally contain no volatile components, being fully polymerisable, and produce quite acceptable films for printing and overprint varnish applications used at present.

There are, however, several drawbacks with current commercial formulations including:-

- 1. High cost of suitable resins, monomers and photoinitiators.
- 2. Surface inhibition by oxygen, requiring amines / benzophenone additions to counteract this problem, and this thereby leads to odour and discoloration.
- 3. Hydrophobic properties of these resin systems, prevents the use of water for viscosity reduction and wash-up.
- 4. Being 100% polymerisable, the absence of volatile solvents or diluents, make it difficult to formulate semigloss and flat coatings or films of low film weight.
- 3. Difficulty in producing low viscosity compositions, as most components of low viscosity have high draize value and therefore avoided for health reasons.

The present invention has provided a practical system that has overcome most of the above:-

- 1. Hydrophilic and water-thinable to over 50%, permitting its use in high gloss, semigloss and flat films.
- 2. Relatively low cost to manufacture from readily available intermediates, requiring only a short duration, low temperature synthesis process.
- 3. Polymerisable without requiring addition of photoinitiator, and without first requiring removal of the water content in the composition.
- 4. Free from inhibition at the surface by oxygen in the air, when radiation cured.
- 5. Cured films are both water-resistant and relatively solvent-resistant.
- 6. Non hazardous in terms of skin contact, and essentially odour-free.

Each of these advantages has considerable merit alone, but collectively provides a major commercially attractive advance to the technology of radiation cured coatings.

Summary of the invention

Depending on the choice of components, an oligomer amide salt can be produced which will photo-polymerise when exposed to ultra violet radiation without the need for a photoinitiator. We have found other variations of the invention which require very low levels (up to 0.5%) of a conventional photoinitiators to affect polymerisation, yet amine synergists are not required to avoid surface tack or undercure.

Most importantly, all variations of this invention are water soluble, water dilutable or water dispersible and will polymerise after radiation, immediately after application to a surface, without the need to remove the water component, although it follows that curing can be accomplished successfully after drying the water if desired. Furthermore, a valuable feature of these systems is their ability to photo-polymerise to a tack-free water-resistant film, when cured in air, either predried or radiated immediately on application to the surface. This full surface cure is normally only achieved in conventional radcure systems by including an amine synergist together with an aromatic ketone in the formulation, and these form undesirable by-products of strong odour and colour. Alternatively, inert gas surface blanketing must be used, which is costly and troublesome.

Details of resin systems.

This patent will describe several ways to synthesise resin systems with the properties as outlined above, the basic properties of water dispersibility, UV curability, with or with the addition of photoinitiator, non oxygen inhibited and water resistant film property after cure. A number of syntheses have proved to be viable.

One system (example 1) is produced by the partial esterification of a difunctional liquid epoxy resin with acrylic or methacrylic acid, which is carried out in the normal way, and this intermediate is then reacted with ethanolamine or diethanolamine or dipropanolamine, to amidify the remaining glycidal groups. This so formed "hybrid "oligomer is inherently hydrophilic and water dispersible. If this resin or its aqueous dispersion, is then treated with acrylic or methacrylic acid, a cationic water-soluble salt is formed between the amide groups of the resin and the acrylic acid. The salt permits much further water dilution. The acid is so firmly bound to the oligomer system, that the resin is rendered odour free. Moreover, the acrylic or methacrylic acid groups will be capable of polymerising to produce a matrix of acid polymer, and also to co-polymerise with acrylate ester groups on the oligomer, yet still retaining the original salt ionic bonds, and thereby achieving water resistance in the cured film.

When subjected to UV radiation, polymerisation rapidly occurs without the need to dry the included water and under normal curing conditions forms a "tack-free" surface at the air interface. There are two important aspects to this process. Firstly, that polymerisation is initiated without the need for a specific photoinitiator to be present, and secondly that oxygen inhibition is apparently avoided, the resultant dry film is tack free and water-resistant. These films will withstand more than 20 wet rubs with water or MEK immediately after cure, and withstand soaking in cold water for 24 hours. Photoinitiators can be added in small amounts to accelerate the rate of cure.

This unique property of self-initiation can be attributed to the influence of N atoms adjacent to carbonyl groups on one side, and the double bond on the other. This dual electron induced activation produces a highly excited state at the double bond, which will produce a free radical on expose to UV energy, and allow oxygen to add to these sites as a peroxy radical, assisting in the propagation process. It has also been suggested that the included water may provide a barrier to block oxygen from the propagating radicals, preventing quenching, and thus contribute to a full surface cure.

A second approach was through the modification of a urea (example 2), or melamine (example 3), formaldehyde condensation oligomer. The UF or MF condensate is reacted with a low MW alcohol to form an ether modified resin, which is water soluble, and this is treated with

acrylic acid to similarly form an amide / salt. This aqueous salt solution, so formed, was found to also share the UV cure properties and produce a viable water-resistant non-tacky film after radiation. A related resin (example 4) was prepared from the condensation product of urea and glyoxal, the acid salt was found to react and cure by UV radiation as above.

A third approach (example 6) was from resin systems produced by the Michael addition of a dialkanolamine to a mono or di-functional acrylic monomer followed by salt formation to the tertiary amine so formed, with acrylic or other unsaturated acid. Although these systems were found to require small additions of conventional photoinitiator to polymerise by UV radiation, a blend with one of the above two resin systems produced satisfactory cure without the need of the photoinitiator. Another system (example 5) was prepared by condensing propylene oxide with diethanolamine and then salt formation as before. This system exhibited partial cure when irradiated with UV.

The above systems are not intended to be a complete list of viable resin systems covered by the patent. Other intermediates are under investigation, viz. dissocyanate / alkanolamine adducts, vinyl and divinyl monomer / dialkanolamine Michael addition products and unsaturated ester alkanolamine condensation products, each then used to form a salt with an ethylenically unsaturated acid to impart the required water solubility, and these also are expected to UV cure.

Example 1

To 0.1mole (36gm of bisphenol A diglycidyl ether (Araldite 6010) is added varying amounts of acrylic acid together with 0.1g hydroquinone monomethyl ether inhibitor and 0.5g catalyst. The mixtures are reacted at 110 C for 40 minutes and then cooled to 95 C, and diethanolamine is added over several minutes, allowing the subsequent exotherm to proceed to 140–150 C with no external heat. The product is allowed to cool to 90 C, and water is then added with rapid stirring producing a white stable dispersion. Acrylic acid is then added slowly with continuous stirring to solublise the resin solution.

After 15 mins, the solution is allowed to cool, inhibitor added and transferred to a dark glass container.

No	DGEBPA	Acrylic Acid	Diethanolamine	Water	Acrylic Acid	Visc
NP63	36g (0.1mol)	5.8g (0.08mol)	12.6g (0.12mol)	20g	10g	>1p
NP64	36g (0.1mol)	6,5g (0.09mol)	11.5g (0.11mol)	20g	7g	>lp
NP65	36g (0.1mol)	7.2g (0.10mol)	10.5g (0.10mol)	20g	6g	420cp
NP66	36g (0.1mol)	7.9g (0.11mol)	9.5g (0.09mol)	20g	6g	980ср
NP67	36g (0.1mol)	8.6g (0.12mol)	8.4g (0.08mol)	20g	5g	110ср
NP68	36g (0.1mol)	9.4g (0.13mol)	7.4g (0.07mol)	20g	6 g	620ср
NP69	36 (0.1mol)	10.1g (0.14mol)	6.3g (0.06mol)	20g	4g	>1p

Each sample was then coated onto calendered paper at 0.2micron using a wire wound applicator, and passed under UV light at 15m/minute. Each film was examined for gloss, surface tack, hardness, water and MEK resistance. The results were as follows:-

NP65, NP66 and NP67 all cured after one pass to give satisfactory films NP63 and NP64 were difficult to apply due their viscosity and required two passes to cure. NP 68 and NP69 were slightly turbid and produced dull films.

Other preparations were made from monofunctional epoxides, by similar reactions except the half acrylic ester was step was omitted, and the full diethanolamine adduct was formed, followed by salt formation with acrylic acid. Six typical examples were made from cresol glycidyl ether, butanediol glycidyl ether, C12-14 alkyl glycidyl ether, neodecanoic acid diglycidyl ester, as well as butanediol di glycidyl ether and an alicyclic diepoxy carboxylate. These all exhibited some of the desirable properties as indicated above, yet were all of lower viscosity and less water resistant.

Example 2

A urea-formaldehyde resin is prepared by reacting urea (one mole) with formalin (37% CHCO, two moles) with a base catalyst (diethylamine). This reaction proceeds rapidly at 50 C rising to 70 C and then when the exotherm diminishes a low MW alcohol (eg propanol 2 moles) added and reacted to etherify the UF resin. After cooling to 60 C, acrylic acid (2 moles) is added and held for 30 minutes. The resin mixture is the allowed to cool with stirring. The odour of acrylic acid rapidly diminishes, indicating that a salt is produced, and this is in the form of a clear, water-soluble liquid resin of medium viscosity. When cast down as a film on a metal, paper or timber surface and immediately passed through UV radiation tunnel, the films are cured and non tacky. Subsequent tests confirm that they are cured and water and solvent resistant.

Example 3

Similar resins were prepared from melamine (1 mole, 126g) in water, with paraformaldehyde (3 moles, 90 g) followed by addition of acrylic acid to produce the amino salt as above. This resin solution was similar to the urea based system, is water soluble and exhibited the same UV cure capability, and was water and solvent resistant.

Example 4

Urea (1 mole, 60 g) was reacted with Glyoxal (1 mole, 145 g of a 40% solution) and then acrylic acid (2 moles, 144 g) added to form a salt. The resultant solution was capable of UV cure but the so formed film was water sensitive.

Example 5

One mole of propylene oxide (58g) was carefully added to one mole (105g) of diethanolamine, and allowed to cool. Water (20g) was added and then one mole (72g) of acrylic acid. The adduct was tested as before and found to be water soluble, low odour and colour, low viscosity but only partially cures under UV radiation.

Example 6

One mole of tri propylene glycol diacrylate (300g) was mixed with one mole (105g) of diethanolamine and heated to 105 C and held for 30 minutes. The product was then cooled to 90 C and 90g water added with stirring. I moles of acrylic acid was slowly added. On testing for cure, this resin was found to cure only with 1-2% of photoinitiator (Irgacure 184)

Example 7

To the resin NP65 as described in example 1, 20% of aqueous pigment dispersions based on carbon black, diarylide yellow and phthalocyanine blue were added with stirring. These pigmented compositions were stable and when cast out as films and exposed to UV radiation, cured in a similar manner to the unpigmented resins previously described. The presence of pigment adversely affects the rate of cure, and small additions of photo-initiator were needed to accelerate the cure.

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